

## Solid State NMR Studies of the Aluminum Hydride Phases

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### ABSTRACT

Several solid state NMR techniques including magic-angle-spinning (MAS) and multiple-quantum (MQ) MAS experiments have been used to characterize various AlH<sub>3</sub> samples. MAS-NMR spectra for the <sup>1</sup>H and <sup>27</sup>Al nuclei have been obtained on a variety of AlH<sub>3</sub> samples that include the β- and γ- phases as well as the most stable α-phase. While the dominant components in these NMR spectra correspond to the aluminum hydride phases, other species were found that include Al metal, molecular hydrogen (H<sub>2</sub>), as well as peaks that can be assigned to Al-O species in different configurations. The occurrence and concentration of these extraneous components are dependent upon the initial AlH<sub>3</sub> phase composition and preparation procedures. Both the β-AlH<sub>3</sub> and γ-AlH<sub>3</sub> phases were found to generate substantial amounts of Al metal when the materials were stored at room temperature while the α-phase materials do not exhibit these changes.

### INTRODUCTION

In order to meet U.S. DOE hydrogen storage goals proposed for years 2010 and 2015, metal hydrides will need to be composed mainly of light elements (i.e., Li, B, Mg, Al, etc.). With a hydrogen gravimetric capacity over 10 wt.%, AlH<sub>3</sub> would be an extremely attractive hydrogen storage material for low temperature fuel cells if its hydrogen absorption and desorption properties could be improved. At least three distinct polymorphic AlH<sub>3</sub> phases can be produced by organometallic synthesis methods [1] where the most thoroughly investigated and stable polymorph is denoted as α-AlH<sub>3</sub>. Recently Sandroock, et al. [2] demonstrated that enhanced thermal decomposition from nearly 30-year old α-AlH<sub>3</sub>, which had been originally made by Dow Chemical, could be achieved by ball milling and doping this powder with LiH. Subsequently, various alane phases (e.g., α, β, and γ) were freshly prepared by Graetz, et al. [3,4] and their desorption kinetics measured over a range of temperatures. Phase composition was found to have significant impact on the stabilities and reaction rates for these samples [2 – 4]. Although the crystal structure for α-AlH<sub>3</sub> had been determined previously [5], the structures for the β- and γ- phases are still unknown as are the locations of the Al and H atoms in these latter phases. In order to understand these kinetic properties as well as various thermodynamics and hydrogen storage behavior, additional fundamental structural and chemical bonding information is needed. One powerful and versatile technique for obtaining such insights in metal hydrides is solid state nuclear magnetic resonance (NMR) [6].

The only prior NMR measurements on AlH<sub>3</sub> samples appears to have been performed over several decades ago using continuous wave and low-resolution pulse methods by Zogal and co-workers [7 -9] who obtained spectra for <sup>27</sup>Al and <sup>1</sup>H nuclei in α-AlH<sub>3</sub>. These NMR experiments

indicated that  $\text{AlH}_3$  is a covalent compound as no observable chemical or Knight shifts [6] were observed for either  $^{27}\text{Al}$  or  $^1\text{H}$  nuclei and any atomic motion was much too slow near ambient temperatures to influence either relaxation times or the rigid lattice line shapes. However, the proton spectra had a very sharp component that these authors attributed to molecular hydrogen ( $\text{H}_2$ ) adsorbed on the hydride particle surfaces [8]. From the acknowledgments in the NMR papers to a published study by Baranowski and Tkacz [10], the single source of alane used in all those prior NMR experiments [7-9] was from the same batch and bottle of Dow made  $\alpha\text{-AlH}_3$  material recently used by Sandrock, et al. [2]. The present work presents newly measured high-resolution NMR spectra on both the old Dow and freshly made  $\text{AlH}_3$  samples with differing phase compositions.

## EXPERIMENTAL

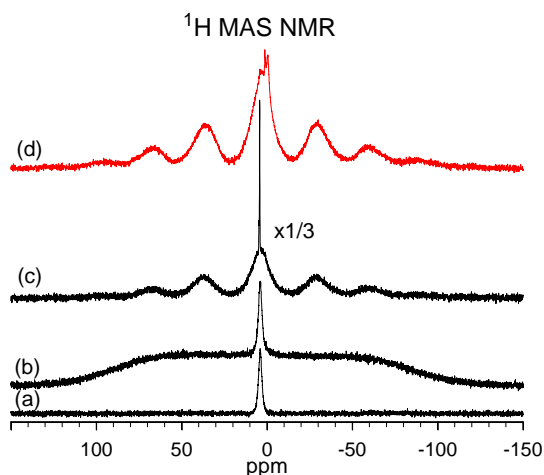
The alane (i.e.,  $\text{AlH}_3$ ) materials were either originally manufactured by the Dow Chemical Company (denoted as “Dow” sample) in the 1970s or recently prepared at Brookhaven National Laboratory (these BNL samples are denoted by the H29XY numbers). The general synthesis methods and procedures described by Brower, et al. [1] were followed as reported previously [3-5]. Powder x-ray diffraction was used to identify the initial phase compositions of the samples. The Dow material was primarily the  $\alpha$ -phase with 8.3wt.% hydrogen content that was virtually unchanged after ~30 years storage in air at ambient conditions. All sample handling was performed in glove boxes under argon atmospheres.

The solid state magic angle spinning nuclear magnetic resonance (MAS-NMR) measurements were performed using a Bruker Avance 500 MHz spectrometer with a wide bore 11.7 T magnet and using a Bruker 4mm probe. The resonance frequencies were 500.23 MHz and 130.35 for protons ( $^1\text{H}$ ) and aluminum ( $^{27}\text{Al}$ ) nuclei, respectively. The  $\text{AlH}_3$  samples were packed into a 4-mm  $\text{ZrO}_2$  rotor in an argon atmosphere glove box and sealed with a tight fitting Kel-F cap. Dry nitrogen gas was used for sample spinning. All MAS-NMR experiments were performed at room temperature unless otherwise noted. Typical  $^{27}\text{Al}$  MAS-NMR spectra were obtained with 14-15 kHz spinning rates after 0.5  $\mu\text{s}$  ( $<\pi/12$  pulse) single pulse and with application of strong  $^1\text{H}$  decoupling pulse of the two-pulse phase modulation (TPPM) scheme [11]. The multiple quantum (MQ) MAS experiment was performed using the z-filter method [12,13] and a 2D spectrum was presented after a shearing transformation. The shifts ( $\sigma$ ) in parts per million (ppm) of the  $^1\text{H}$  and  $^{27}\text{Al}$  peaks are externally referenced to tetramethylsilane (TMS) and 1.0 M of  $\text{Al}(\text{NO}_3)_3$  aqueous solution, respectively.

## RESULTS AND DISCUSSION

The static and MAS  $^1\text{H}$  NMR spectra of the Dow- $\text{AlH}_3$  sample are shown in Fig. 1 (a)-(c), and MAS spectrum of  $\alpha\text{-AlH}_3$  sample from BNL (H2963) is also shown in Fig. 1-(d). Since the same Dow material is being used in these measurements that was studied previously by Zogal, et al. [7-9] except for separate storage for ~20 years at BNL, static NMR spectra (Fig. 1-(a) and (b)) are consistent with the previous observations [7-9], including two proton components with distinctively different line widths (i.e., 1.3 kHz vs 90 kHz) and relaxation times (~0.1s vs 70 s). The broad line is from the protons in the rigid  $\text{AlH}_3$  lattice while the narrow line is attributed to the molecular hydrogen ( $\text{H}_2$ ) presumably generated by decomposition of the hydride (see below). The MAS method with a spinning rate of 14.5 kHz greatly reduces the line width (over 10-20

times) (Fig. 1-(c)), so that isotropic chemical shifts could be better determined. A single peak at 4.4 ppm with FWHM of 130 Hz was observed for hydrogen gas. The position of the center band of  $\text{AlH}_3$  peak was about 3.0 ppm and its width was as wide as 5.5 kHz due to strong  $^1\text{H}$ - $^1\text{H}$  dipole coupling that could not be averaged out under the current spinning speed. A very similar MAS alane spectrum was observed for newly synthesized BNL material (see Fig. 1-(d)), but without the narrow component at  $\sim 4.4$  ppm from  $\text{H}_2$ . The weak and sharp components seen at  $\sim 1.5$  ppm are due to residual organic solvents from the synthetic process. The present MAS-NMR results suggest that the Dow material has only slightly decomposed over its  $\sim 30$  years of storage (i.e.  $\sim 3.2\%$  of total proton content is as  $\text{H}_2$ ) and it still exhibits considerable stability under ambient conditions.

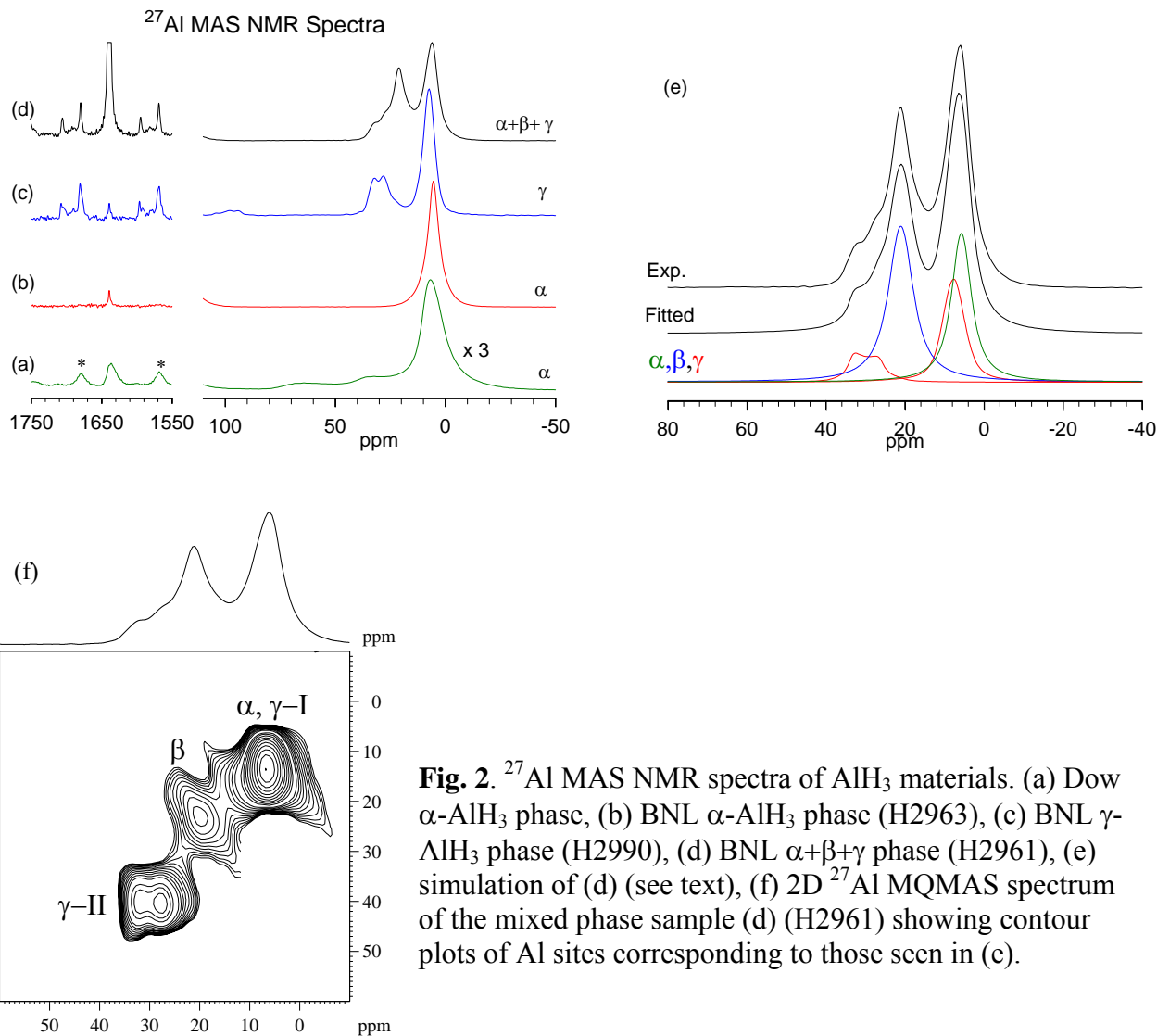


**Fig. 1.** Static and MAS  $^1\text{H}$  NMR spectra of the Dow (a-c) and the BNL (d) aluminum hydride ( $\alpha\text{-AlH}_3$ ). (a) static,  $d1=1$  s, (b) static,  $d1=300$  s, (c) MAS (14.5 kHz),  $d1=300$  s, (d) MAS (14.5 kHz),  $d1=300$  s, where  $d1$  is the repetition delay time during signal averaging.

between 0-30 ppm in  $^{27}\text{Al}$  MAS spectra represent the central transition ( $m=-1/2 \leftrightarrow m=+1/2$ ) of  $^{27}\text{Al}$  ( $I=5/2$ ) nuclei in different alane phases. These peaks show  $T_1$  relaxation time in 4-6 sec range for all materials. All spectra were carefully examined using short repetition delay time  $d1$  that could enhance the signal strength of fast relaxing  $\text{Al}_2\text{O}_3$  type peaks in the 30 - 70 ppm region. For example, Fig. 2-(a) show such resonances when using  $d1=0.1$  s. The other spectra were acquired with full relaxation delays ( $d1=40$ s). The spinning side bands (not shown) are widely distributed over 4000 ppm depending on the size of quadrupole interaction of  $^{27}\text{Al}$  nuclei, and they are associated with satellite transitions, i.e.  $m=\pm 3/2 \leftrightarrow m=\pm 1/2$  and  $m=\pm 5/2 \leftrightarrow m=\pm 3/2$ . The envelopes of spinning side band intensities were later used during the fitting of the powder patterns to extract the quadrupole coupling constant ( $C_Q$ ) and the asymmetry parameter ( $\eta$ ) [14]. These quadrupole parameters as well as the isotropic chemical shifts allowed us to characterize the coordination geometry around Al atoms. A peak at  $\sim 1640$  ppm was observed for all the samples we studied, indicating the presence of metallic aluminum ( $\text{Al(M)}$ ) [15-17] from varying amounts of  $\text{AlH}_3$  self decomposition at room temperature. Note that spinning side bands of  $\text{AlH}_3$  phases are also seen around the  $\text{Al(M)}$  peak except the BNL  $\alpha\text{-AlH}_3$  sample which shows small quadrupole coupling ( $C_Q \sim 0.2$  MHz, see below). The mixed phase ( $\alpha+\beta+\gamma$ ) show relatively a strong initial  $\text{Al(M)}$  peak even for freshly prepared sample compared to the others, implying that degradation is occurring much more rapidly with this combination of  $\text{AlH}_3$  phases.

Fig. 2-(e) shows the deconvoluted  $^{27}\text{Al}$  line shapes of three different structural phases and fitting of a spectrum (Fig. 2-(d)) for the mixed phase ( $\alpha+\beta+\gamma$ ) material. A 2D MQMAS spectrum

(see Fig. 2-(f)) reveals higher resolution of all these sites supporting the assignments. Spectra of pure compounds  $\alpha$  and  $\gamma$  were first fitted to obtain quadrupole parameters using the QUASAR software [18] and spectrum Fig. 2-(d) was used to extract them for the  $\beta$  phase as well as quantitatively estimate each component in the H2961 sample. The quadrupole parameters are



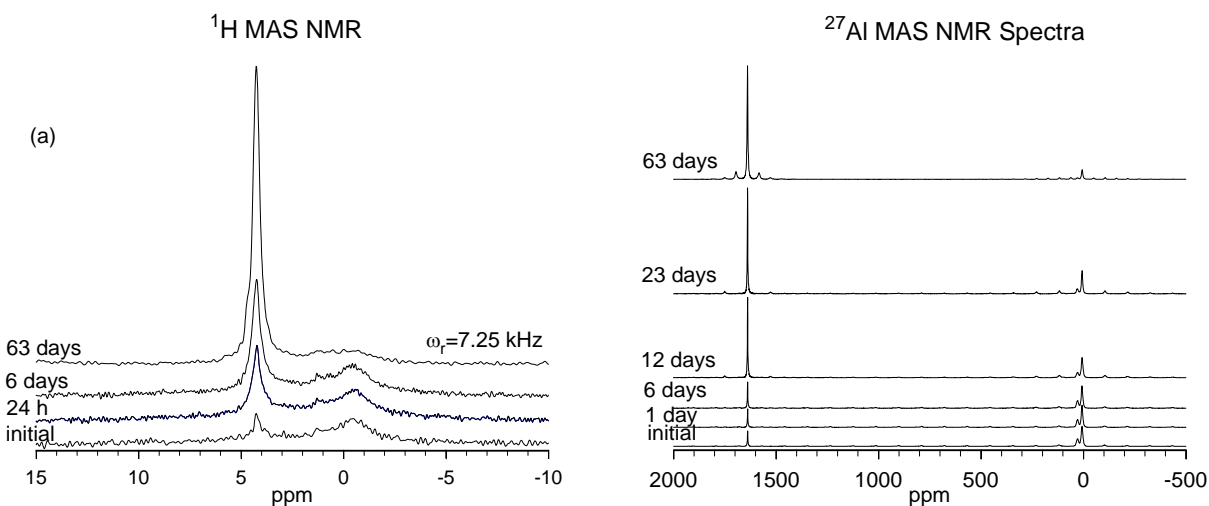
**Fig. 2.**  $^{27}\text{Al}$  MAS NMR spectra of  $\text{AlH}_3$  materials. (a) Dow  $\alpha$ - $\text{AlH}_3$  phase, (b) BNL  $\alpha$ - $\text{AlH}_3$  phase (H2963), (c) BNL  $\gamma$ - $\text{AlH}_3$  phase (H2990), (d) BNL  $\alpha+\beta+\gamma$  phase (H2961), (e) simulation of (d) (see text), (f) 2D  $^{27}\text{Al}$  MQMAS spectrum of the mixed phase sample (d) (H2961) showing contour plots of Al sites corresponding to those seen in (e).

compiled in Table 1. Both  $\alpha$  and  $\beta$  phases show weak quadrupole coupling constants, indicating the Al atoms are in more symmetric environments that induce very minor electric field gradient. In contrast, the quadrupole coupling constants found for both  $^{27}\text{Al}$  peaks in  $\gamma$ - $\text{AlH}_3$  appear to be about 10 times higher than the spectra in the  $\alpha$  and  $\beta$  phases, suggesting that these Al sites in  $\gamma$ - $\text{AlH}_3$  have quite different geometries. It is also noted that the site occupancy ratio (2:1) between  $\gamma$ -I and  $\gamma$ -II peaks in the pure  $\gamma$ -alane sample [H2990] was different from the mixed phases of H2961 (see Table 1). However, the estimated quadrupole parameters need further refinements to provide more accurate ratios. This analysis work is currently in progress.

The self-decomposition reaction ( $\text{AlH}_3 \rightarrow \text{Al(M)} + 3/2\text{H}_2$ ) at room temperature was studied by acquiring  $^1\text{H}$  and  $^{27}\text{Al}$  MAS signals as a function of time for various  $\text{AlH}_3$  materials. Once packed under Ar atmosphere, a  $\text{ZrO}_2$  NMR rotor with a tight sealing Kel-F cap was used over three month period for NMR measurements and storage under  $\text{N}_2$  gas. Fig. 3 shows  $^1\text{H}$  (a) and

**Table 1.** The Quadrupole coupling parameters.

Sample	code	$\delta_{\text{iso}}$ (ppm)	$C_Q$ (MHz)	$\eta$	Ratio
$\alpha$ - $\text{AlH}_3$	BNL H2963	5.8	0.25	0.1	
$\gamma$ - $\text{AlH}_3$	BNL H2990	$\gamma$ -I: 10.9	2.9	0.55	0.48
		$\gamma$ -II: 36.0	4.2	0.3	1.0
$\beta$ - $\text{AlH}_3$	from BNL H2961	21.5	0.38	0.38	$\alpha:\beta:\gamma\text{-I}:\gamma\text{-II}=0.22:0.36:0.031:0.11$



**Fig. 3.** (a)  $^1\text{H}$  MAS NMR spectra obtained in the course of decomposition of  $\gamma$ - $\text{AlH}_3$  under Ar atmosphere at room temperature, (b) the corresponding  $^{27}\text{Al}$  MAS NMR spectra showing both resonances of  $\text{AlH}_3$  and  $\text{Al(M)}$ .

$^{27}\text{Al}$  (b) MAS NMR results of the  $\gamma$ - $\text{AlH}_3$  material. Growth of the 4.4 ppm peak in  $^1\text{H}$  NMR spectra (Fig. 3-(a)) over the reaction period is well synchronized with growth of  $\text{Al(M)}$  peak at 1640 ppm in  $^{27}\text{Al}$  NMR spectra (Fig. 3-(b)) and decrease of  $\text{AlH}_3$  peaks at  $\sim 0$  ppm. These results provide *in-situ* observations of the self decomposition process due to unstable nature of these hydrides at room temperature. The high resolution NMR method also allows us to extract some details about which phase degrade more quickly when similar experiments were performed for pure  $\alpha$  and the mixed phase sample H2961. Total decomposition was observed for  $\gamma$ - $\text{AlH}_3$  and H2961 while the  $\alpha$  phase samples prepared at BNL have stabilities very similar to the old Dow material. These measurements will be reported elsewhere. Note this approach for NMR kinetics study of decomposition reaction has led to some inconvenient rotor ruptures during our MAS experiments due to enormous pressure build up of  $\text{H}_2$  gas inside the closed rotor.

## CONCLUSIONS

Static and MAS NMR techniques have been efficiently applied to characterize various  $\text{AlH}_3$  samples. From the analyses of  $^{27}\text{Al}$  MAS NMR spectra, NMR characterization of structures of three different crystalline phases,  $\alpha$ ,  $\beta$  and  $\gamma$ - $\text{AlH}_3$ , were made for the first time. Unlike  $\alpha$  and  $\beta$  phases, the  $\gamma$  phase was found to consist of two distinct sites with the occupation ratio 2:1 and with distorted coordination geometries compared to the other two phases. Faster decomposition of the  $\gamma$  phase at room temperature, which was monitored by both  $^1\text{H}$  and  $^{27}\text{Al}$  MAS NMR, represents a greater instability than for  $\alpha$ - $\text{AlH}_3$  that was also found in recent decomposition studies at elevated temperature [3,4,19], and the result may be correlated with distorted geometry in  $\gamma$ - $\text{AlH}_3$ . The stability of the  $\alpha$  phase was also confirmed for the new BNL materials while independent stability check of the  $\beta$  phase was not performed in this work.

## ACKNOWLEDGMENTS

This research was partially performed at the Jet Propulsion Laboratory, which is operated by the California Institute of Technology under contract with the NASA. This work was partially supported by DOE through Award #DE-AI-01-05EE11105. The NMR facility at Caltech was supported by the National Science Foundation (NSF) under Grant Number 9724240 and partially supported by the MRSEC Program of the NSF under Award Number DMR-0080065. This work was supported at BNL by the DOE under contract DEA-AC0298CH100886.

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